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(54) PRODUCTION OF POLYESTER HAVING LONG METHYLENE CHAIN

(57)Abstract:
PURPOSE: To obtain an aromatic polyester which exhibits a liquid crystal behavior due to the orientation of polymer at a low temperature by reacting a specified esterified aromatic dicarboxylic acid compound having a long methylene chain with a diol.
CONSTITUTION: An aliphatic alcohol (e.g. Unilin 425, a product of Toyo Petrolite Co.) having a molecular weight of 350 to 1,000 is reacted with a cyclic acid anhydride (e.g. trimellitic anhydride) to produce an esterified aromatic dicarboxylic acid compound having a long methylene chain. The obtained dicarboxylic acid compound is then reacted with a diol to give a polyester. An aromatic or aliphatic diol can be used as the diol. Examples of aromatic diol used include hydroquinone and bisphenol A. Examples of aliphatic diol used include ethylene glycol and butane diol. The obtained polyester is useful as, e.g. a component of an adhesive and an additive for improving the activity of a plastic.

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CLAIMS

[Claim(s)]
[Claim 1] The manufacture approach of the polyester in which the aromatic series dicarboxylic acid and diols which have the ester group of the long-chain methylene chain length who makes with an or more 350 molecular weight [or less 1000] fatty alcohol and a cyclic anhydride come to react are made to come to react.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] Since this invention has a long-chain methylene chain, in the case of all the aromatic polyester of the shape of the property of a wax, and a rod, it relates to the manufacture approach of the useful polyester which can also have a thermotropic liquid crystal property.
[0002]
[Description of the Prior Art] The wax is widely used for the physical-properties regulator of the lubricant of rubber processing in a plastics list, a release agent, and adhesives etc., and low-molecular-weight polyethylene wax, a micro crystallin wax, its paraffin wax, etc. are common. However, the effectiveness of a wax will fade according to volatilization, elution, etc. at the time of a prolonged activity for low-molecular, or it will be lost. The wax of the amount of macromolecules is demanded for such a reason. By giving the Para object structure, by giving a rod-like gestalt, aromatic polyester can give liquid crystallinity and gives high intensity polyester. Generally this is called engineer NINGU plastics and known well. In order to perform spinning and molding under an elevated temperature 200 degrees C or more generally, the very expensive facility was required. Molding processing under lower temperature conditions was desired.
[0003]
[Problem(s) to be Solved by the Invention] The object of this invention is offering the polyester to which orientation of the polymer can be carried out at comparatively low temperature with the combination of a monomer.
[0004]
[Means for Solving the Problem] This invention offers the polyester to which make the aromatic series dicarboxylic acid and diols which have the ester group of the long-chain methylene chain length who makes with an or more 350 molecular weight [or less 1000] fatty alcohol and a cyclic anhydride come to react come to react.
[0005] The fatty alcohol of this invention is fatty alcohol of the shape of the with an or more 350 molecular weight [or less 1000] shape of a straight chain, and branching.
[0006] As a cyclic anhydride, you may be a tricarboxylic acid anhydride, a tetracarboxylic acid anhydride, and the other carboxylic anhydrides of many **. Specifically trimellitic anhydride and anhydrous — 1, 4, and 5-naphthalene tricarboxylic acid — anhydrous — 2, 6, 7-naphthalene tricarboxylic acid, and anhydrous — 3, 3', and 4-diphenyl tricarboxylic acid — Anhydrous 3, 3', 4-benzophenone tricarboxylic acid, 1 and 3, 4-cyclopentane tricarboxylic acid, Anhydrous 2, 2', 3-diphenyl tricarboxylic acid diphenylsulfone -3, 3', 4-tricarboxylic acid, diphenyl isopropylidene -3, 3', 4-tricarboxylic acid, and anhydrous — 3, 4, and 10-propylene tricarboxylic acid — ethylene tricarboxylic acid, pyromellitic dianhydride, an anhydrous BIFUTARU acid, and anhydrous — 3, 3', 4, and 4' - benzophenone tetracarboxylic acid — The anhydrous bicyclo [2, 2, 2] oct-5-en -2, 3-dicarboxylic acid, Anhydrous bicyclo [2, 2, 2] oct-7-en - 2, 3, 5, 6-tetracarboxylic acid, anhydrous 1, 2 and 6, 7-xanthone tetracarboxylic acid, and anhydrous — 1, 2, 6, 7-thio KISATON tetracarboxylic acid, and anhydrous — 1, 2, 6, and 7-anthraquinone tetracarboxylic acid anhydrous perylene tetracarboxylic acid etc. can be illustrated.
[0007] Composition of the dicarboxylic acid monomers which have long-chain methylene chain length's ester group can be obtained by the usual esterification reaction of fatty alcohol and a cyclic anhydride. An intermediary's temperature exceeding the melting point of fatty alcohol, i.e., 50 degrees C - 200 degrees C, is desirable on reaction temperature conditions. Moreover, since alcohol can also serve as a reaction solvent, it is compoundable with a non-solvent, but in order to control a reaction rate, you may react in an organic solvent. By the esterification reaction, the derivative of the para position or the meta position is obtained for the location of the carboxyl group of for example, anhydrous benzene tetracarboxylic acid. In order to control the orientation of the obtained polymer, separation purification of the Para object and a meta-object is desirable. Since using the Para object and meta-object mixture for the usual polyester composition without purification separation can skip a purification process, it is desirable.
[0008] As diols, the diols of aromatic series or aliphatic series can be used. As aromatic series diol, there are hydroquinone, biphenol, bisphenol A, Bisphenol F, Bisphenol B, a screw (4-hydroxyphenyl) sulfone, screw (4-hydroxyphenyl) methane, the screw (4-hydroxyphenyl) ether, screw (3-hydroxyphenyl) methane, the screw (3-hydroxyphenyl) ether, screw (2-hydroxyphenyl) methane, the screw (2-hydroxyphenyl) ether, etc. It is usable, if it is not limited to this and is by diols, although there are ethylene glycol, triethylene glycol, butanediol, hexandiol, a diethylene glycol, polyethylene diol, polyester diol, polybutadiene diol, etc. as aliphatic series diol. Moreover, the glycerol which has the hydroxyl group of three organic functions depending on the case is usable.

[0009] This obtained polyester can be used as oxidization, the component of adhesives, the activity amelioration additive of plastics, a pigment dispersing element and the pigment-content powder assistant of a resin masterbatch, and a compatibility grant agent of various ingredients. It can mix with general polymers, such as polystyrene, a polyvinyl chloride, polyethylene, polypropylene, polyester, a polyamide, and a polyether, and can also use. Moreover, it is also possible to use as a distributed assistant of two or more kinds of polymers with bad dispersibility.
[0010]
[Example] Hereafter, an example explains this invention. The section expresses weight among an example. Synthetic pyromellitic dianhydride of example 1 dicarboxylic acid [A] 19 section uni-phosphorus 425 (Oriental PETORO light company make, number average molecular weight 460, fatty alcohol) Heating churning of the 81 section above-mentioned mixture was carried out at 120 degrees C for 5 hours. The terminal point of a reaction was checked because there is no absorption of the acid anhydride of 1780cm-1 near [an infrared absorption spectrum]. As a result of the infrared absorption spectrum, since a product had absorption of the ester group of 1730cm-1, and absorption of the carboxyl group of 1704cm-1, it was a reactant ester compound, and it was the low solid-state of opalescence with a melting point of 80 degrees C.
[0011]
The synthetic dicarboxylic acid of polyester [A] 17.5 section biphenol 2.8 section PARATORU en sulfonyl chloride 7.4 section picoline Temperature up was slowly carried out to 100 degrees C, agitating the 60 section above-mentioned mixture, and, subsequently it was made to react at the temperature of 100 degrees C for about 5 hours. The product carried out precipitation purification with the methanol, and removed the solvent. The result of gel permeation chromatography (GPC) to the number average molecular weight of the obtained aromatic polyester was about 3000. Liquid crystal behavior could observe the obtained polyester at 90 degrees C with the heating mold polarization microscope, and it turned out that orientation of the polymer is carried out. Moreover, even if it cooled, the orientation was held and the behavior as the same liquid crystal polyester as the general poly propine was checked.
[0012] Synthetic pyromellitic dianhydride of example 2 dicarboxylic acid [B] 13 section uni-phosphorus 700 (Oriental PETORO light company make, number average molecular weight 700, fatty alcohol) The 87 sections [0013] Heating churning of the above-mentioned mixture was carried out at 120 degrees C for 5 hours. The terminal point of a reaction was checked because there is no absorption of the acid anhydride of 1780cm-1 near [an infrared absorption spectrum]. The product was the low solid-state of opalescence with a melting point of 95 degrees C. The synthetic dicarboxylic acid of polyester [B] 24.3 section biphenol 2.8 section PARATORU en sulfonyl chloride 7.4 section picoline Temperature up was slowly carried out to 100 degrees C, agitating the 60 section above-mentioned mixture, and, subsequently it was made to react at the temperature of 100 degrees C for about 5 hours. The product carried out precipitation purification with the methanol, and removed the solvent. The result of gel permeation chromatography (GPC) to the number average molecular weight of the obtained aromatic polyester was about 3500. Orientation of the obtained polyester was carried out at 110 degrees C with the heating mold polarization microscope, and liquid crystal behavior has been observed. Moreover, even if it cooled, the orientation was held and liquid crystal behavior was checked.
[0014] Example 3 dicarboxylic-acid [C] composition trimellitic anhydride 21.5 section uni-phosphorus 700 (Oriental PETORO light company make, number average molecular weight 700, fatty alcohol) Heating churning of the 78.5 section above-mentioned mixture was carried out at 120 degrees C for 5 hours. The terminal point of a reaction was checked because there is no absorption of the acid anhydride of 1780cm-1 near [an infrared absorption spectrum]. The product was the low solid-state of opalescence with a melting point of 95 degrees C.
The synthetic dicarboxylic acid of a polymer [C] 23.9 section biphenol 2.8 section PARATORU en sulfonyl chloride 7.4 section picoline Temperature up was slowly carried out to 100 degrees C, agitating the 60 section above-mentioned mixture, and, subsequently it was made to react at the temperature of 100 degrees C for about 5 hours. The product carried out precipitation purification with the methanol, and removed the solvent. The result of gel permeation chromatography (GPC) to the number average molecular weight of the obtained aromatic polyester was about 2500. The liquid crystal behavior according the obtained polyester to the orientation of a polymer was observable at 110 degrees C with the heating mold polarization microscope. Moreover, even if it cooled, it turned out that the orientation is held.
[0015] The synthetic pyromellitic dianhydride of example 4 dicarboxylic acid [D] The 9.5 section uni-phosphorus 425 (Oriental PETORO light company make, number average molecular weight 460, fatty alcohol) 40.5 section xylene Heating churning of the 50 section above-mentioned mixture was carried out at 100 degrees C for 5 hours. The terminal point of a reaction was checked because there is no absorption of the acid anhydride of 1780cm-1 near [an infrared absorption spectrum]. It cooled to the room temperature and the product removed the solvent in vacuum oven. The obtained aliphatic series ester was a white low solid-state with a melting point of 80 degrees C. Moreover, when polyester was compounded like the example 1 and biphenol was used, predetermined aromatic polyester was obtained. Number average molecular weight was about 3200. That the liquid crystal behavior by the orientation of a polymer is shown has checked the polyester of this invention with the polarization microscope. The synthetic result of other polyester was combined and was shown in the following table.
[0016]
Polyester composition result ---------- Acid anhydride Alcohol Diol Liquid crystal-ized temperature (degree C)
---------- BT The uni-phosphorus 425 BP 90 BT The uni-phosphorus 550 BP 100

BT The uni-phosphorus 700 BP 110 TA The uni-phosphorus 425 BP 110 TA The uni-phosphorus 700 BP 110 BT The uni-phosphorus 425 BA - TA Uni-phosphorus 425BA -BT The uni-phosphorus 425 EG - TA Uni-phosphorus 425 EG - ---------- BT: Anhydrous benzene tetracarboxylic acid, TA: Anhydrous benzene tricarboxylic acid BP : [Bisphenol,] BA: — bisphenol A EG: — ethylene glycol uni--- phosphorus 425:MW=460 -- uni--- phosphorus 550:MW=550 -- uni--- phosphorus 700:MW=700 liquid crystal-ized temperature: — polarization was applied with the heating mold polarization microscope, and the visual judgment of the color tone was carried out.

[0017]

[Effect of the Invention] By this invention, the polyester which has long-chain in a side chain was able to obtain. Furthermore, the aromatic polyester in which the liquid crystal behavior originating in the orientation of the same polymer as liquid crystal polyester is shown at low temperature was able to obtain by using diol like biphenol.

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